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## Interactions between Volatile Reduced Sulfur Compounds and Metals in the Seine Estuary (France)

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### Abstract:

Concentrations of volatile hydrogen sulfide (H<sub>2</sub>S), carbonyl sulfide (OCS), methane thiol (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) in the Seine estuary (France) were investigated in spring 2005 using samples collected from the first meter beneath the surface. Levels of dissolved metals (Ag, Cd, Cu, Zn, Ni, Co, Pb), suspended particulate matter, and particular organic carbon were also assessed. Maximum concentrations were 0.80 nM for H<sub>2</sub>S, 0.64 nM for OCS, 3.06 nM for MeSH, 11.06 nM for DMS, and 1.18 nM for DMDS, and different features were observed for the five volatile reduced sulfur compounds (VRSCs). Experiments were conducted to determine silver–VRSC conditional stability constants. Major interactions were observed between H<sub>2</sub>S and Ag, which may partially account for the absence of volatile H<sub>2</sub>S at the lowest salinities. OCS, MeSH, and DMS did not interact with Ag, as revealed by their insignificant *K'* values. Variations in concentrations along the salinity gradient may be explained by the influence of phytoplanktonic compounds.

**Keywords:** Seine estuary - Volatile reduced sulfur compounds - Metal - Conditional stability constant

## 42 **Introduction**

43 The Seine river rises on the Plateau of Langres in Burgundy and flows northwest into  
44 the English Channel at Le Havre, situated at the mouth of the 160-km long Seine estuary  
45 (Fig 1) whose upstream limit is marked by Poses Dam. The Rouen and Havre regions  
46 have become heavily industrialized over the last century (currently representing 40% of  
47 French industry) and are home to about 25% of the French population. The RNO  
48 (National Monitoring Network) previously revealed significant metal contamination in  
49 mussels along the Normandy coasts, with silver and cadmium concentrations several  
50 orders of magnitude higher than the lowest concentrations recorded in France during the  
51 same period (Chiffolleau et al. 2001 and 2005).

52 The SEINE AVAL scientific program was launched on the basis of this knowledge, to  
53 identify – among many other tasks - the origin of metals in the Seine river catchment  
54 are, evaluate their fluxes in the marine environment, measure their concentrations along  
55 the salinity gradient and model their biogeochemical behaviour in the estuary. Previous  
56 studies have already demonstrated the remobilization of particulate silver and particulate  
57 cadmium of freshwater origin in the mixing zone (Thouvenin et al. 2004) and hence  
58 their potential availability for marine organisms (Thouvenin et al. 2005).

59 Hydrogen sulfide ( $H_2S$ ) is produced by the anaerobic decomposition of organic matter  
60 via sulfate reduction (Dyrssen and Kremling 1990) and is a constituent of anoxic marine  
61 environments at concentrations up to micromolar level.  $H_2S$  also exists in photic zones  
62 of oligotrophic to eutrophic waters (Luther and Tsamakis 1989; Cutter and Krahforst  
63 1998). Walsh et al. (1994) additionally showed that phytoplankton species can produce  
64 hydrogen sulfide in oxic waters. A major source of  $H_2S$  in oceans appears to be the  
65 hydrolysis of carbonyl sulfide (Elliot et al. 1989). Carbonyl sulphide (OCS) is the most

66 abundant and probably the most long-lived sulfur gas in the atmosphere (Ulshöfer and  
67 Andreae 1998). OCS production is based on two main processes: the photochemical  
68 degradation of dissolved organo-sulfur compounds (Zepp and Andreae 1994) and dark  
69 production (non-photochemical) from dissolved organo-sulfur compounds or sediment  
70 (Flock and Andreae 1996). Dimethyl sulphide (DMS, “CH<sub>3</sub>SCH<sub>3</sub>”), methane thiol  
71 (MeSH, “CH<sub>3</sub>SH”) and dimethyl disulfide (DMDS, “CH<sub>3</sub>SSCH<sub>3</sub>”) are synthesized from  
72 the same precursor: dimethylsulfoniopropionate (DMSP; Kiene and Taylor 1988;  
73 Tanzer and Heumann 1992). This molecule is released into the water column during  
74 phytoplankton degradation through grazing by zooplankton, senescence and cell  
75 leaking, and is subsequently converted into sulfur compounds by enzymatic cleavage or  
76 demethylation (Simo et al. 2002).

77 Many metals (e.g., Ag, Cd, Pb) and some transition metals (e.g., Cu, Co, Zn, Ni), such  
78 as hydrogen sulfide and thiols (Laglera and Van den Berg 2003), tend to interact and  
79 form complexes with soft bases and have affinities with sulfur compounds (Stumm and  
80 Morgan 1981). The conditional stability constant  $K'$  for Ag(I) organosulfur complexes  
81 (e.g., thiols) is about  $\log K' = 13$  (Bell and Kramer 1999). Al-Farawati and Van den Berg  
82 (1999) determined the conditional stability constants of several metal-hydrogen sulfides  
83 in seawater pH 8 at 25°C and revealed possible interactions between metal ions (e.g.  
84 Cu<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>) and H<sub>2</sub>S in the marine environment.

85 No data was available until now on interactions between other volatile reduced sulfur  
86 compounds (OCS, MeSH, DMS and DMDS) and metals, despite the fact that these  
87 compounds exhibit similar complexing properties. In this study, we experimentally  
88 determined conditional stability constants between VRSCs and one soft sphere metal -  
89 Ag<sup>+</sup> - in the aim of pinpointing possible interactions between VRSCs and silver in  
90 aquatic environments. Silver was chosen as the prime candidate in view of its high

91 contribution to Seine estuary contamination. We decided to use the Irving-Williams  
92 (1953) series, which classifies metals according to their affinities  
93 ( $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ ), coupled with knowledge on the conditional stability constants  
94 of  $\text{Ag}^+$ , to assess possible interactions between VRSCs and metals in the Seine estuary.  
95 To achieve this, VRSCs and metal concentrations were measured along the salinity  
96 gradient during the SILVER-2 cruise, and an initial attempt was made to determine  
97 Silver-VRSC conditional stability constants.

## 98 **Materials and Methods**

### 99 **Sampling and *in situ* measurements**

100 The SILVER-2 cruise took place from the May 23 to June 1, 2005 on the R/V Thalia,  
101 equipped with a white room container. Sampling was done along the salinity gradient to  
102 determine variations in VRSCs and metal concentrations in the Seine estuary (Fig 1).  
103 During the 10-day cruise, each estuary station (from Caudebec to offshore of Le Havre)  
104 was sampled twice: once during spring tide (May 23-24) and once during neap tide  
105 (May 30-31). Marine coastal water samples (from Le Havre port to offshore of Dieppe)  
106 were collected from May 25-29 (Fig 1). One sample (named L station) was collected  
107 further offshore (Fig 1, black star) in order to assess VRSC and metal concentrations in  
108 a zone far removed from urban inputs.

109 Various additional parameters (conductivity, sea surface temperature SST, particulate  
110 organic carbon POC and suspended particulate matter SPM) were also determined to  
111 complete our assessment of VRSC distribution along the salinity gradient. Conductivity  
112 and SST measurements were done using a polarographic probe and are available for all  
113 monitored stations (Chiffolleau et al. 2001). Suspended particulate matter (SPM) was

114 collected by water sample filtration (one filter per sample, no replicates) through a pre-  
115 weighted membrane (0.4- $\mu\text{m}$  Nuclepore<sup>®</sup>) under fixed pressure to avoid cell damage  
116 (Chiffoleau et al. 2001). Filtration of another aliquot of water samples through  
117 precombusted glass fiber (0.7  $\mu\text{m}$  GF/F Whatman) filters was performed on board.  
118 These filters were used to measure POC at the shore lab after individual storage in glass  
119 Petri dishes followed by immediate freezing and storage in the dark pending analysis  
120 (Chiffoleau et al. 2001). POC was analysed with a CHN autoanalyser (Carlo Erba  
121 model) after decarbonation by HCl vapour (Chiffoleau et al. 2001). Triplicate filters  
122 were used to improve POC measurement accuracy.

123 Water samples for metal analyses downstream from Tancarville bridge were collected  
124 using an all-Teflon<sup>®</sup> pump (Chiffoleau et al. 1994). Additional water samples were  
125 collected between Vieux Port and Poses, also using clean bottles. All samples were  
126 immediately filtered in the on-board laboratory container, using trace metal-cleaned pre-  
127 weighted filters (0.4- $\mu\text{m}$  Nuclepore<sup>®</sup>; Chiffoleau et al. 1994). The filtered water  
128 subsamples were then preserved in acid-cleaned 250-ml polyethylene bottles and stored  
129 at  $\text{pH} < 1.6$  pending further analysis (Chiffoleau et al. 1994).

### 130 **Volatile Reduced Sulfur Compound analysis**

131 To avoid VRSC sample deterioration, analyses were carried out on board immediately  
132 after collection (less than 15 mins.). Water samples were collected using a clean  
133 polycarbonate bottle (with HCl 0.5N) dipped one meter beneath the sea surface. The  
134 subsample was immediately drawn into a clean syringe to avoid contact with the  
135 atmosphere and ensuing sample contamination. The sample syringes were stored in cool  
136 boxes pending duplicate analysis.

137 The analytical method used was fully described by Cozic et al. (2008) and  
138 simultaneously determines the concentrations of five reduced, naturally volatile (free  
139 and labile) sulfur compounds in a water sample. This method is based on gas  
140 chromatography (GC CP-3800 Varian<sup>®</sup> with a CP-PoraBond Q column), coupled with a  
141 purge and trap system. Briefly, the water sample (15 ml) was injected into the stripping  
142 vessel using the syringe. Sulfur gases were then extracted from the liquid phase and  
143 swept into a cryogenic preconcentrated trap. Once extraction was complete, carrier gas  
144 (helium) was used to sweep the concentrated gases into the chromatographic column.  
145 Using this analytical method, up to 30 water samples were able to be analysed per day  
146 (less than 12 mins. per sample). Moreover, each sample was broken down into one  
147 filtered subsample (0.45 µm, Teflon<sup>®</sup> PTFE) and one unfiltered subsample, in order to  
148 assess sulfur ligand speciation (particulate or dissolved). Gentle positive pressure (<0.1  
149 kg/cm<sup>2</sup>) was applied by hand to minimize cell damage during filtration.

## 150 **Metal analyses**

151 Preconcentration by liquid/liquid extraction of the water samples (Danielsson et al.,  
152 1982) was performed to eliminate signal interference due to the salt matrix and  
153 concentrate the metals present in the sample. This technique is based on the production  
154 of metal complexes with a mixture of APDC and DDDC, their extraction by freon and  
155 subsequent destruction through acidification of the organic phase (Chiffolleau et al.  
156 1994). An ICP-MS was used to determine dissolved metal concentrations (Ag, Cd, Pb,  
157 Cu, Co, Zn, Ni). Quality control and accuracy analysis were performed using certified  
158 international reference material from estuarine waters (SLEW-3 from the NRCC). The  
159 analytical results obtained for dissolved reference material systematically differed from  
160 certified values by less than 10%, and reproducibility was generally better than 6% for

161 all study metals. Quantification limits were 5 pM for Ag, Cd and Pb, 20 pM for Co, 50  
162 pM for Zn, 100 pM for Cu and 300 pM for Ni.

### 163 **Silver complexation by sulfur compounds**

164 Our experimental protocol was based on the mixing of a metal (silver) with a single  
165 volatile sulfur compound (H<sub>2</sub>S, OCS, MeSH or DMS; DMDS standard not available)  
166 dissolved in deionized water to keep the chemical system as simple as possible. Al-  
167 Farawati and Van den Berg (1999) previously demonstrated that the conditional stability  
168 constant between silver and HS<sup>-</sup> ions does not change significantly with salinity. pH was  
169 fixed at ca. 7.7 (with KOH added to the deionized water) for H<sub>2</sub>S and DMS experiments  
170 and ca. 6.5 for OCS and MeSH.

171 Chemical speciation experiments were conducted as follows: an initial, pure solution  
172 (99.99%) of 1 g/L AgNO<sub>3</sub> and 10-ml solutions with Ag concentrations ranging from  
173 zero to 2 or 20 nM were drawn in acid-cleaned (HCl, 0.5 N) syringes. To avoid  
174 photodegradation, the syringes were stored in the dark at room temperature. Volatile  
175 reduced sulfur liquid solutions were then prepared (constant concentration, 2 nM for  
176 H<sub>2</sub>S, OCS, MeSH and 20 nM for DMS) using gaseous or liquid standards. Gaseous  
177 standards were from custom-made sulfur gas bottles (Scott Gas<sup>®</sup>), with certified  
178 concentrations of H<sub>2</sub>S (1.1±0.04 ppm) and DMS (1.1±0.01 ppm). Solubility, depending  
179 on pH, was 0.1 M/atm for H<sub>2</sub>S (Boffi et al. 2000) and 0.63 M/atm for DMS (Barcellos  
180 da Rosa et al. 2003) in deionized water (pH<6, 25°C). The quantity of gas to be injected  
181 into the acid-cleaned syringe was calculated according to Henry's law to obtain the  
182 equivalent targeted VRSC concentration in the liquid phase (deionized water). A  
183 calibrated-release permeation device (VICI-Metronics) was used for OCS. The air  
184 stream flux was calculated on the basis of OCS solubility (K<sub>H</sub>=2.08 M/atm in distilled

185 water; Elliot et al. 1989) to obtain a final 2-nM liquid OCS concentration in the syringe.  
 186 A standard, liquid solution (21% w/w, Aldrich) was diluted to acquire a final 2 - 20 nM  
 187 solution of methane thiol (MeSH). Finally, silver and VRSCs were mixed and an  
 188 additional 10 ml of sulfur-containing solution was added to each syringe containing a  
 189 given silver concentration (e.g., 0 nM, 0.25 nM). All syringes were shaken energetically  
 190 for 2 minutes to mix the solutions and balance the liquid and gas phases, then stored in  
 191 the dark again pending chromatographic analysis. Care was taken to systematically  
 192 maintain the same “contact” time between VRSCs and silver prior to analysis. Final pH  
 193 was ca. 7.7 for the H<sub>2</sub>S and DMS solutions and ca. 6.5 for the OCS and MeSH solutions.  
 194 Binding strength models were based on a multicomponent version of the single 1:1  
 195 complex formation mechanism, which is mathematically identical to the model of  
 196 Langmuirian-type submonolayer adsorption (Ruzic 1996):



198 whereby S is an individual binding site. In the following equations, silver is shown as M  
 199 (for metal) and VRSC is shown as L (for ligand).

200 The distribution of labile species (silver and VRSC) gives the following relationships in  
 201 reference to equation (1):

$$202 \quad M_t = M' + ML, L_t = L' + ML \quad (2)$$

203 whereby M<sub>t</sub> and L<sub>t</sub> represent the total concentrations of metal and ligand, and M' and L'  
 204 represent concentrations of unreacted compounds, i.e. free active sites. The conditional  
 205 stability constant is then defined as follows:

$$206 \quad K' = ML / [(M')(L')] \quad (3)$$

207 With a simple mathematical adjustment to equations (2) and (3), we obtain the  
 208 following equation:

$$209 \quad K' = (L_t - L') / [(M_t \times L') - L' (L_t - L')] \quad (4)$$



210 Using equation (4), which describes the relationship between the conditional stability  
211 constant  $K'$ , concentration of free sulfur active sites  $L'$ , total concentration of sulfur  
212 compound  $L_t$  and total concentration of silver  $M_t$ , we obtained a graphic representation  
213 of the conditional stability constants between silver and the test VRSCs.

214 Equation (4) was then adjusted to a second-degree equation:

$$215 \quad L'^2 + (1/K' + M_t - L_t) \times L' - L_t/K' = 0 \quad (5)$$

216 The concentration of free sulfide active sites was determined for one conditional  
217 stability constant only, and for the selected total concentrations of silver and VRSCs  
218 (equation 5). The results of each speciation experiment will subsequently be compared  
219 with theoretical curves (for a fixed  $K'$ ), to determine if significant interactions exist  
220 between silver and the test VRSCs. To facilitate discussion, conditional stability  
221 constants are represented by their log value ( $\log K'$ ).

## 222 **Results**

### 223 **Supporting parameters**

#### 224 *Suspended particulate matter (SPM) distribution along the salinity gradient*

225 A comparison ( $\chi^2$  test,  $p=0.05$ ) of SPM distribution along the salinity gradient revealed  
226 clear differences (Fig 2) between the two estuary sampling periods, with highest values  
227 recorded during spring tide (May 23-24). However, highest SPM concentrations were  
228 systematically correlated with low salinity (below 10). This SPM profile may indicate  
229 the location of the maximum turbidity zone (MTZ), which is normally situated in the  
230 lowest salinities (salinity 0 to 5, Fig 2, Van den Berg 1993). The clear increase in SPM  
231 concentrations adjacent to salinity 14-18 revealed the location of the mid estuarine

232 maximum zone (MEZ), where trace element mobilization and fluxes from sediments are  
233 stronger (Buggy and Tobin 2006).

#### 234 *Particulate organic carbon (POC) distribution along the salinity gradient*

235 No significant variations in POC distribution ( $\chi^2$  test) were observed in the estuarine  
236 zone between the spring and neap tide sampling cruises (Fig 3). Similarly to SPM  
237 distribution, the highest values occurred with the lowest salinities, with up to 600 mg/L  
238 measured (Fig 3). This value increased in the mid estuarine zone, with  $90.5 \pm 23.3$  mg/L  
239 (n=7) in the 14-20 salinity range. POC concentration decreased in the marine zone, with  
240  $18.1 \pm 10.1$  mg/L (n=15). Relative standard deviation (RSD) for our measurements was  
241 1.4% and 11.4% respectively.

#### 242 **Distribution of VRSCs along the salinity gradient**

243 No significant differences were highlighted between filtered and unfiltered subsamples  
244 according to an  $\chi^2$  test (p=0.05). Moreover, no significant differences ( $\chi^2$  test) in VRSC  
245 concentrations were noted between the spring and neap tide cruises, although volatile  
246 sulfur compound distribution varied along the salinity gradient.

247 Hydrogen sulfide concentrations were below the limit of detection (0.07 nM;  
248 Cozic et al. 2008) up to a salinity of 17.9. In the mid estuary zone, a clear increase in  
249 H<sub>2</sub>S concentrations was observed, followed by a clear decrease at higher salinities (Fig  
250 4A). Carbonyl sulfide concentrations were constant in the upper estuary and decreased  
251 slightly above salinity 18.7 (Fig 4B). Methane thiol, dimethyl sulfide and dimethyl  
252 disulfide showed similar profiles along the salinity gradient, i.e. a gradual increase to  
253 maximum value at mid-salinity range, followed by a decrease. This pattern was  
254 particularly marked for DMS and DMDS (Fig 4C, 4D, 4E).

## 255 **Determination of Silver-VRSC conditional stability constants**

256 The H<sub>2</sub>S conditional stability constant was determined by comparing experimental data  
257 with theoretical curves and gave a log K' value greater than 12. This is similar to the  
258 results obtained by Al-Farawati and Van den Berg (1999) using sea water pH, therefore  
259 supporting our method for determining VRSC conditional stability constants with a  
260 given metal. Other tested reduced sulfur compounds (OCS, MeSH and DMS) did not  
261 appear to have a strong affinity with silver. Free OCS (purgeable with helium) did not  
262 interact strongly with increasing silver concentrations, and a conditional stability  
263 constant K' of between 0.1 and 0.01 – and hence a very low log K' (≈0) - was observed.,  
264 The same trend was observed for MeSH, with a very low conditional stability constant  
265 notwithstanding the initial MeSH concentration (K' of about 0.05 (log K'≈0)). An  
266 absence of interactions between DMS and Ag<sup>+</sup> was also shown with metal  
267 concentrations between zero and 20 nM. However, when silver concentrations were  
268 increased to 4 μM (experimental value), a slight decrease (ca. 20%) was observed in  
269 free DMS concentrations. We therefore concluded that the conditional stability constant  
270 K' (Ag)DMS was 0.75x10<sup>-4</sup> (log K'≈0), which is insignificant in view of observed silver  
271 concentrations. These preliminary experiments demonstrated that only H<sub>2</sub>S appears to  
272 interact strongly with silver in aquatic environments. OCS and MeSH had a low affinity  
273 with silver and no interaction was observed with DMS.

## 274 **Metal distribution along the salinity gradient**

275 The metals monitored during the SILVER-2 cruise were silver (Ag), cadmium (Cd),  
276 lead (Pb), copper (Cu), cobalt (Co), zinc (Zn) and nickel (Ni). Only silver concentrations  
277 were monitored during both cruises (May 23-24 and May 30-31; Fig 5A); remaining

278 metals were measured during the second cruise (Figure 5B-C). Silver and cadmium  
279 concentrations increased in the estuarine zone from zero to ca. 13-15 and decreased  
280 rapidly at the highest salinities (Fig 5A, 5B). Cobalt showed a relatively constant  
281 concentration ( $1.1 \pm 0.2$  nM, n=12) along the salinity gradient (Fig 5B). Nickel and  
282 copper distribution showed the same trend, with a slight decrease along the salinity  
283 gradient (Fig 5C). Zn concentrations clearly decreased along the salinity gradient  
284 (Fig 5C) after reaching a maximum near salinity 6.

## 285 **Discussion**

### 286 **Distribution of DMS, DMDS and MeSH along the salinity gradient**

287 Dimethyl sulfide, dimethyl disulfide and methane thiol concentrations clearly increased  
288 with salinity (Fig 4C-E). Phytoplankton density and POC distribution were positively  
289 correlated in the Seine estuary (Chiffoleau et al. 2001) and phytoplankton density was  
290 shown to be constant along the salinity gradient, with a relatively constant POC value  
291 from zero to salinity ca. 24 (Fig 3). Sciare et al. (2002) previously demonstrated that  
292 DMS increased with salinity in the Gironde estuary (France), correlated with the  
293 distribution of *Phaeocystis* and *Dinophyceae*, which are recognized as being high  
294 producers of DMSP (Liss et al. 1997). Lemaire et al. (2002) revealed the mid estuarine  
295 maximum zone to be highly reactive in terms of phytoplankton (organic matter)  
296 degradation. The distribution of DMS, DMDS and MeSH in the Seine river may  
297 therefore be accounted for by a shift in phytoplanktonic population from low DMS  
298 producers such as diatoms in the upstream estuary, to high DMS producers further  
299 downstream. Unfortunately, pigment data is unavailable for the SILVER-2 cruise.

300 In comparison to other European estuaries (Sciare et al. 2002), DMS concentrations in  
301 the Seine river are very high, with maximum values greater than 10 nM adjacent to  
302 salinity 25 (Fig 4D). The mean concentration ( $8.2\pm 4.5$  nM;  $n=52$ ) measured in the Seine  
303 estuary is double that of the Rhine (Germany) and about ten times higher that of  
304 Gironde (France) (0.7 nM; Sciare et al. 2002). These results suggest a significant  
305 production of DMS in the estuarine plume, but cannot be further explained due to a lack  
306 of quantitative data on DMSP and phytoplankton species. In the marine zone (above 30-  
307 salinity), DMS concentrations were similar to those determined by Turner et al. (1988)  
308 in sea water around mainland Britain, and by Walker et al. (2000) on the continental  
309 shelf. No other estuarine DMDS measurements have been conducted to date, hence  
310 making comparison with our data impossible. The relatively slow decrease in MeSH  
311 concentrations versus DMS and DMDS in marine waters may be due to consumption by  
312 bacterioplankton, which use MeSH for amino acid synthesis (Kiene et al. 2000). The  
313 constant MeSH concentrations observed above salinity 25 (Fig 4C) were put down to an  
314 increase in bacterial growth, which induces DMSP degradation in MeSH (Kiene and  
315 Taylor 1988). The clear decrease in DMS and DMDS concentrations in shelf waters  
316 may be due to dilution with upper estuarine waters, or mixing with older, oceanic water  
317 masses containing less DMS and DMDS than MeSH (Fig 4D-E). In conclusion,  
318 additional work clearly appears necessary to improve our understanding of DMS and  
319 DMDS increases in the plume versus the marine zone, and comprehend the high DMS  
320 values measured in the estuary.

### 321 **Distribution of OCS along the salinity gradient**

322 OCS concentrations were higher in estuarine waters (mean value,  $0.5\pm 0.3$  nM,  $n=50$ )  
323 than in shelf waters (mean value,  $0.3\pm 0.1$  nM,  $n=47$ ) (Fig 4B), as previously observed

324 by Sciare et al. (2002) in the Rhine estuary (Germany), Watts (2000) in Yarmouth  
325 estuary (UK), and Cutter and Knoery (1993) in two estuaries in the eastern United  
326 States. The production of OCS in surface waters is thought to be controlled by  
327 photochemical processes, which depend on photosensitizer concentrations (Zepp and  
328 Andreae 1994), which in turn are related to phytoplankton concentrations (Kettle et al.,  
329 2001). The Seine estuary is a eutrophicated region, receiving significant organic inputs  
330 from the continent (Chiffoleau et al. 2001). The high OCS concentrations observed at  
331 low salinities could therefore be related to the microbial degradation of organic sulfur  
332 compounds (Andreae and Ferek 1992). The photo-destruction of methane thiol could be  
333 another source of carbonyl sulfide in the Seine river (Flock and Andreae 1996). In  
334 addition, light penetration generally decreases with rising SPM concentrations near  
335 salinity 14 (Smith and Baker 1979), therefore increasing OCS production by  
336 photodegradation. However, OCS release from sediment to overlying waters may be  
337 another major source in the estuarine environment, in particular in the mid estuarine  
338 zone (Zhang et al. 1998). The surface water distribution of OCS in the Seine river is  
339 hence likely to be influenced by sulfur gas fluxes from sediment, due to the estuary's  
340 relative shallowness (mean depth 10 m). This could also explain the constant  
341 concentrations observed in the upper estuary (up to salinity 17.9), although no porewater  
342 data is available to estimate sedimentary OCS concentrations. Similarly to DMS and  
343 DMDS, the clear concentration decrease from salinity ca. 18 downwards could well be  
344 due to the mixing of high CDOM concentrations in estuarine waters and lower CDOM  
345 concentrations in seawater (less organisms).

## 346 **Distribution of H<sub>2</sub>S along the salinity gradient**

347 No volatile sulfides (free sulfide and labile metal-sulfide complexes) were observed at  
348 the lowest salinities (Fig 4A), whereas significant concentrations of carbonyl sulfide and  
349 others VRSCs were measured, suggesting the presence of major H<sub>2</sub>S removal  
350 mechanisms. Oxidation induced by higher oxygen levels in the upper estuarine zone  
351 (Chiffoleau et al. 2001), complexation with particulate trace metals, or metal sulfide  
352 precipitation may explain the absence of free H<sub>2</sub>S between salinity zero and 17.9. Rozan  
353 et al. (1999) similarly found no free sulfide in four southern New England rivers and  
354 suggested that this was due to metal sulfide complexes. Elliot et al. (1989) pointed out  
355 that the complexation of trace oceanic metals with bisulfide (S<sup>2-</sup>) and sulfide ions (HS<sup>-</sup>)  
356 should impact the amount of volatile H<sub>2</sub>S in the water column. In view of its high  
357 conditional complexation constant with sulfide (log K'(Ag)=11.6; Al-Farawati and Van  
358 den Berg 1999), silver probably affects the percentage of free sulfide in the Seine  
359 estuary (Fig 4A). However, silver concentrations (Fig 5A) were very low compared to  
360 sulfide concentrations (Fig 4A) and the high interaction of silver with organic ligands  
361 (Luoma et al., 1995) and chloride suggests that silver cannot be responsible for the  
362 absence of free HS<sup>-</sup> in the upper estuarine zone. The high concentrations of copper  
363 found in the estuary (Fig 5C) and copper's high conditional complexation constant with  
364 bisulfide ions (log K'=12.9; Al Farawati and Van den Berg 1999) may also influence  
365 sulfide distribution in the estuary. Similarly to H<sub>2</sub>S-Zn complexes, H<sub>2</sub>S-Cu complexes  
366 are kinetically inert to dissociation (Luther et al. 1996); as a result, the absence of free  
367 sulfide (HS<sup>-</sup> ions) in the upper estuarine zone may be due to strong interactions with  
368 copper. Cadmium, lead and cobalt metals do not appear to play a significant role in H<sub>2</sub>S  
369 distribution in the Seine estuary in view of their weak interactions with sulfide (Al-  
370 Farawati and Van den Berg 1999) and the low concentrations measured (Fig 5B).

371 Although zinc and nickel concentrations were high in the upper estuarine zone (Fig 5C),  
372 their very low conditional complexation constants for bisulfide ions (Al-Farawati and  
373 Van den Berg 1999) mean they do not influence H<sub>2</sub>S distribution. The presence of  
374 powerful metal "ligands" probably explains the absence of free sulfide in the upstream  
375 Seine. This theory has already been put forward by Cutter and Krahforst (1988), who  
376 showed that sulfide may impact the cycles of several trace metals via the formation of  
377 stable complexes at concentrations of less than 1 nM, hence causing free sulfide  
378 concentrations in the water column to decrease considerably.

379 The increased SPM concentrations in the mid estuary zone (Fig 2) coincided with an  
380 abrupt increase in hydrogen sulfide (Fig 4A), which may be linked to sedimentary  
381 sulfide releases (Luther and Tsamakis 1989). Sediments are capable of scavenging metals  
382 that interact with sulfide, hence increasing free sulfide concentrations in surface waters.  
383 As no differences were observed in H<sub>2</sub>S concentrations in filtered and unfiltered  
384 samples, we concluded that SPM does not play a key role in H<sub>2</sub>S distribution along the  
385 salinity gradient. Carbonyl sulfide hydrolysis may be highest in the mid estuarine  
386 maximum zone (MEZ), therefore explaining the presence of H<sub>2</sub>S from salinity 18.9  
387 upwards (Fig 4A-B). Moreover, the high degradation of organic matter (e.g.  
388 phytoplanktonic cells) observed in the MEZ may create anoxic microzones, leading to  
389 sulfate reduction and hydrogen sulfide production. Our current state of knowledge does  
390 not provide quantitative data on these H<sub>2</sub>S sources. Similarly to the other VRSCs, the  
391 clear decrease in sulfide concentrations in the marine zone is related to fresh water  
392 dilution in the English Channel.

## 393 **Conclusion**

394 **No** significant interactions were shown between OCS and silver, MeSH and silver and  
395 DMS and silver. Variations in biogenic sulfur MeSH, DMS and DMDS compound  
396



397 distribution may be linked to phytoplankton speciation, with an increase in high DMSP-  
398 producers near salinity 20. The significant OCS concentrations observed in the Seine  
399 estuary were related to various processes: dissolved organic sulfur compound  
400 photodegradation, methane thiol degradation and OCS diffusion from sediment (in the  
401 mid estuarine zone). Although silver may interact with bisulfide ions even at low  
402 concentrations, this did not explain the undetectable H<sub>2</sub>S levels observed below salinity  
403 14. The clear increase in sulfide concentrations at the highest salinities was related to an  
404 increase in sulfide sources (flux from sediments, hydrolysis of OCS and phytoplankton  
405 degradation), plus the presence of others metal complexation mechanisms (e.g.  
406 sedimentary scavenging). H<sub>2</sub>S may be stabilized in the MEZ by oxygen depletion.

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408

#### 409 **Acknowledgments**

410 The SILVER 2 cruise was funded by the Seine Aval 3 program, which has been  
411 contributing to improving knowledge on the Seine estuary for several years. We would  
412 also like to thank the R/V Thalia crew for their precious technical assistance during the  
413 10-day cruise.

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## References

- Al-Farawati, R. and C.M.G. Van den Berg. 1999. Metal-Sulfide complexation in seawater. *Mar. Chem.* 63: 331-352.
- Andreae, M.O. and R.J. Ferek. 1992. Photochemical production of carbonyl sulfide in seawater and its emission to the atmosphere. *Global Biogeochem. Cy.* 6: 175-183.
- Barcellos da Rosa, M., W. Behnke and C. Zetzsch. 2003. Study of the heterogeneous reaction of O<sub>3</sub> with CH<sub>3</sub>SCH<sub>3</sub> using the wetted-wall flowtube technique. *Atmos. Chem. Phys.* 3: 1665-1673.
- Bell, R.A. and J.R. Kramer. 1999. Structural chemistry and geochemistry of silver-sulfur compounds: critical review. *Environ. Toxicol. Chem.* 18: 9-22.
- Boffi, A., M. Rizzi, F. Monacelli and P. Ascenzi. 2000. Determination of H<sub>2</sub>S solubility via the reaction with ferric hemoglobin I from the bivalve mollusk *Lucina Pectina*. *Biochim. Biophys. Acta* 1523: 206-208.
- Buggy, C.J. and J.M. Tobin. 2006. Seasonal and spatial distributions of tributyltin in surface sediment of the Tolka estuary, Dublin, Ireland. *Env. Poll.* 143: 294-303.
- Chiffolleau, J.F., D. Cossa, D. Auger and I. Truquet. 1994. Trace metal distribution, partition and fluxes in the Seine estuary in low discharge regime. *Mar. Chem.* 47: 145-158.
- Chiffolleau, J.F., D. Auger, E. Chartier, P. Michel, I. Truquet, A. Ficht, J.L. Gonzalez and L.A. Romana. 2001. Spatio-temporal changes in cadmium contamination in the Seine estuary (France). *Estuaries* 24: 1029-1040.
- Chiffolleau, J.F., D. Auger, N. Roux, E. Rozuel and A. Santini. 2005. Distribution of silver in mussels and oysters along the french coasts: Data from the national monitoring program. *Mar. Pollut. Bull.* 50: 1713-1744.
- Cozic, A., J. Radford-Knoery, B. Averty and E. Viollier. 2008. Simultaneous analysis of five volatile reduced sulfur compounds by purge and cryogenic trapping/gas chromatography separation in natural waters. *Submitted*.
- Cutter, G. A. and C.F. Krahfurst. 1988. Sulfide in Surface Waters of the Western Atlantic Ocean. *Geophys. Res. Lett.* 15 (12): 1393-1396.
- Danielsson, L.-G., B. Magnusson, S. Westerlund and K. Zhang. 1982. Trace metal determinations in estuarine waters by electrothermal atomic absorption spectrometry after extraction of dithiocarbamate complexes into freon. *Anal. Chim. Acta* 144: 183-188.

448 Dyrssen, D. and K. Kremling. 1990. Increasing hydrogen sulfide concentration and trace  
449 metal behavior in the anoxic Baltic waters. *Mar. Chem.* 30: 193-204.

450 Elliot, S., E. Lu and S. Rowland. 1989. Rates and mechanisms for the hydrolysis of  
451 OCS in natural waters. *Environ. Sci. Technol.* 23: 458-461.

452 Flock, O.R. and M.O. Andreae. 1996. Photochemical and non-photochemical formation  
453 and destruction of OCS and MeSH in ocean waters. *Mar. Chem.* 54: 11-26.

454 Irving, H. and R.J.P. Williams. 1953. The stability of transition-metal complexes. *J.*  
455 *Chem. Soc.* 637: 3192-3220.

456 Kettle, A.J., T.S. Rhee, M. Von Hobe, A. Poulton, J. Aiken and M.O. Andreae. 2001.  
457 Assessing the flux of volatile sulfur gases from the ocean to the atmosphere. *J.*  
458 *Geophys. Res.* 106: 12193-12209.

459 Kiene, R.P. and B.F. Taylor. 1988. Biotransformation of organosulfur compounds in  
460 sediments via 3-mercaptopropionates. *Nature* 332: 148-150.

461 Laglera, L.M. and C.M.G. Van den Berg. 2003. Copper complexation by thiols  
462 compounds in estuarine waters. *Mar. Chem.* 82: 71-89.

463 Lemaire, E., G. Abril, R. De Wit and H. Etcheber. 2002. Distribution of phytoplankton  
464 pigments in nine European estuaries and implications for an estuarine typology.  
465 *Biogeochemistry* 59: 52-23.

466 Liss, P.S., A.D. Hatton, G. Malin, P.D. Nightingale and S.M. Turner, 1997. Marine  
467 Sulfur emissions. *Philos. T. Roy. Soc.* 352: 159-169.

468 Luther, G.W. and E. Tsamakis. 1989. Concentration and form of dissolved sulfide in the  
469 oxic water column of the ocean. *Mar. Chem.* 27, 165-177.

470 Luther, G.W., D. Rickard, S.M. Theberge and A. Olroyd. 1996. Determination of metal  
471 (bi)sulfide stability constants of  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  by  
472 voltammetric methods. *Environ. Sci. Technol.* 30: 671-679.

473 Ruzic, I. 1996. Trace metal complexation at heterogeneous binding sites in aquatic  
474 systems. *Mar. Chem.* 53: 1-15.

475 Rozan, T.F., B. Gaboury and G.W. Luther. 1999. Measuring Metal Sulfide complexes in  
476 oxic river waters with square wave voltammetry. *Env. Sc. Tech.* 33: 3021-3026.

477 Sciare, J., N. Mihalopoulos and B.C. Nguyen. 2002. Spatial and temporal variability of  
478 dissolved sulfur compounds in European estuaries. *Biogeochem.* 59: 121-141.

479 Simo, R., S.D. Archer, C. Pedros-Alios, L. Gilpin and C.E. Stelfox-Widdicombe. 2002.  
480 Coupled dynamics of dimethylsulfoniopropionate and dimethylsulfide cycling and  
481 the microbial food web in surface waters of the North Atlantic. *Limnol. Oceanogr.*  
482 47: 53-61.

483 Smith, R.C. and K.S. Baker. 1979. Penetration of uv-b and biologically effective dose-  
484 rates in natural waters. *Photochem. Photobiol.* 29: 311-323.

485 Stumm, W. and J. Morgan. 1981. *Aquatic Chemistry. An introduction emphasizing*  
486 *chemical equilibria in natural waters.* John Wiley and sons, New York. 780 pages.

487 Tanzer, D. and KG. Heumann. 1992. Gas chromatographic trace-level determination of  
488 volatile organic sulfides and selenides and of methyl iodide in Atlantic surface  
489 water. *Inter. J. Environ. An. Ch.* 48, 1: 17-31.

490 Thouvenin, B., B. Boutier, J.F. Chiffolleau, J.L. Gonzalez, L.A. Romana, D. Auger, B.  
491 Averty, E. Chartier, S. Crochet and I. Truquet. 2004. Contribution à l'étude de la  
492 dynamique et de la spéciation des contaminants. Rapport d'activité 2003.  
493 Programme Seine Aval 2. Thème Analyse des risques chimiques et  
494 microbiologiques.

495 Thouvenin, B., B. Boutier, J.F. Chiffolleau, J.L. Gonzalez, D. Cossa, D. Auger, B.  
496 Averty, E. Rozuel-Chartier, D. Menard, A. Santini and M. Olivier. 2005.  
497 Contribution à l'étude de la dynamique et de la spéciation des contaminants.  
498 Rapport d'activité 2004. Programme Seine Aval 2. Thème Morphodynamique,  
499 cycle des vases et contaminants associés.

500 Ulshöfer, V.S. and M.O. Andreae. 1998. Carbonyl Sulfide (COS) in the Surface Ocean  
501 and the Atmospheric COS budget. *Aquat. Geochem.* 3: 283-303.

502 Van den Berg, C.M.G. 1993. Complex formation and the chemistry of selected trace  
503 elements in estuaries. *Estuaries* 16: 512-520.

504 Walker, C.F., M.J. Harvey, S.J. Bury and F.H. Chang. 2000. Biological and physical  
505 controls on dissolved dimethyl sulfide over the north-eastern continental shelf of  
506 New Zealand. *J. Sea Res.* 43: 253-264.

507 Watts, S.F. 2000. The mass budget of carbonyl sulfide, dimethyl sulfide, carbon  
508 disulfide and hydrogen sulfide. *Atmos. Environ.* 34: 761-779.

509 Zepp, R.G. and M.O. Andreae. 1994. Factors affecting the production of OCS in  
510 seawater. *Geophys. Res. Lett.* 21: 2813-2816.

511 Zhang, L., R.S. Walsh and G.A. Cutter. 1998. Estuarine cycling of carbonyl sulfide:  
512 production and sea-air flux. *Mar. Chem.* 61: 127-142.

513 **Figure captions**

514

515 Figure 1 – Study sites: the Seine estuary and English Channel coast. Marine stations were  
516 located between Le Havre port (salinity 26) to offshore of Dieppe (salinity 33).  
517 Estuarine stations extended from Caudebec (salinity 0) to offshore of Le Havre  
518 (salinity 30). The black star represents the sample station furthest from urban  
519 inputs (salinity 33.5).

520

521 Figure 2 - Distribution of Suspended Particulate Matter (SPM) along the salinity gradient  
522 from May 23 to June 1, 2005.

523

524 Figure 3 - Distribution of particulate organic carbon along the salinity gradient from May 23  
525 to June 1, 2005.

526

527 Figure 4 - Distribution of VRSCs along the salinity gradient from May 23 to June 1, 2005.

528 Estuarine stations had salinity in the 0.6-29.5 range. Marine stations had salinity in the

529 25.2-33.5 range. A, H<sub>2</sub>S ; B, OCS ; C, MeSH ; D, DMS ; E, DMDS. Analytical

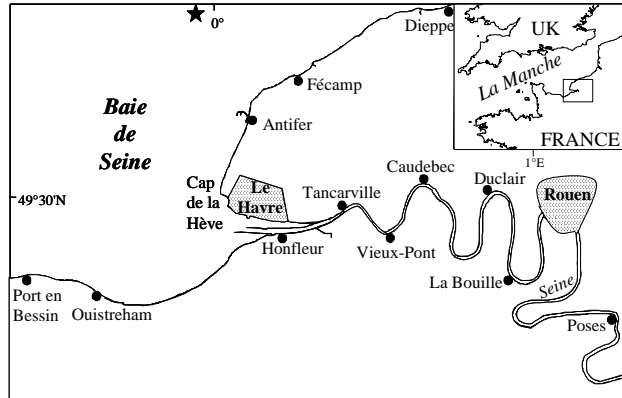
530 accuracy is 6.0% for H<sub>2</sub>S, 4.1% for OCS, 5.6±% for MeSH, 4.9% for DMS and 8.4% for

531 DMDS (Cozic et al. 2008).

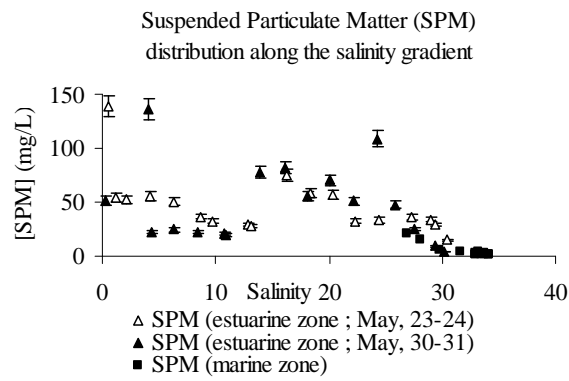
532 Figure 5 - Distribution of dissolved metals along the salinity gradient from May 23 to June 1,  
533 2005. A: dissolved silver; B: Cd, Pb and Co; C: Zn, Ni and Cu.

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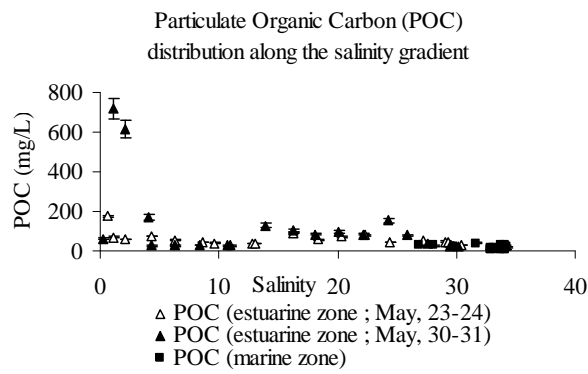
535 Figure 1 –



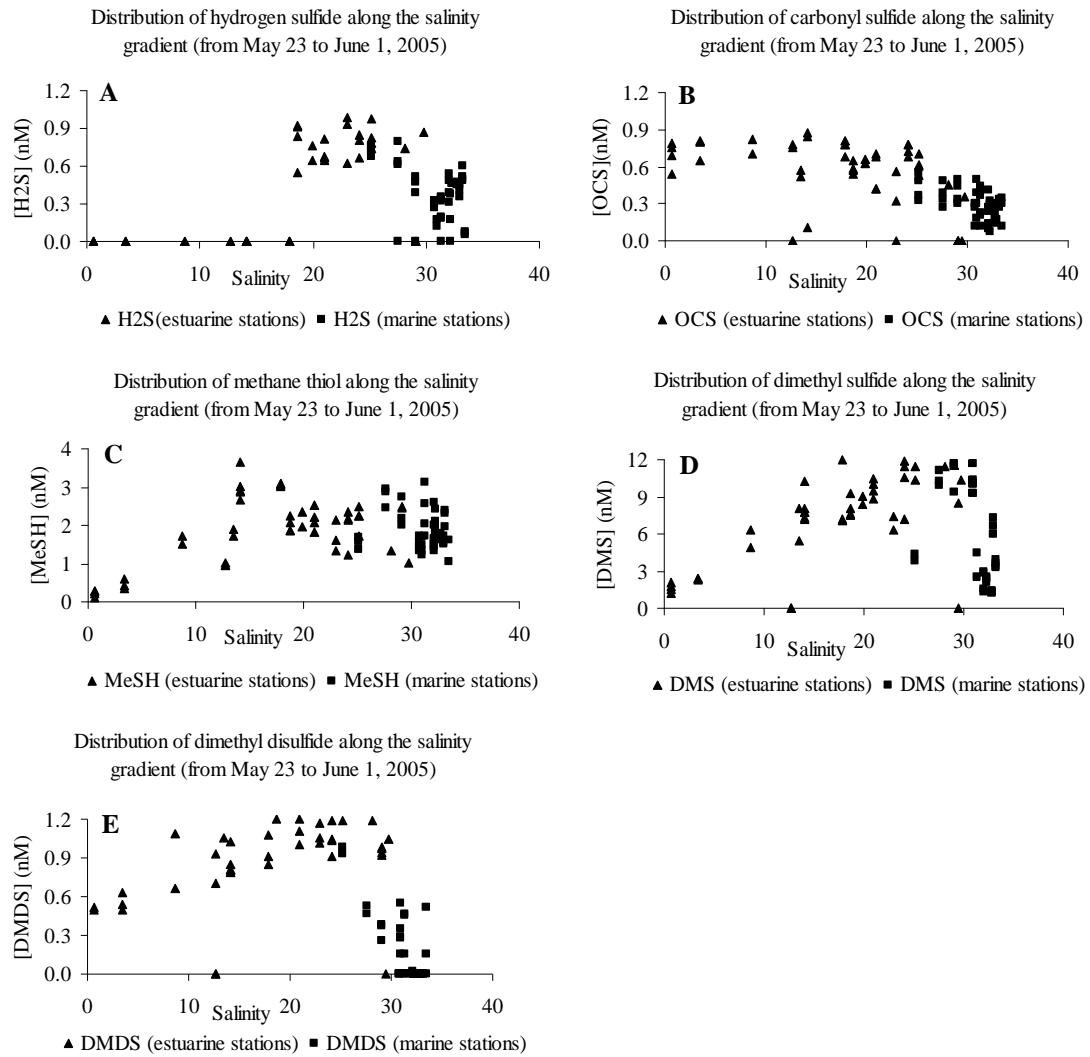
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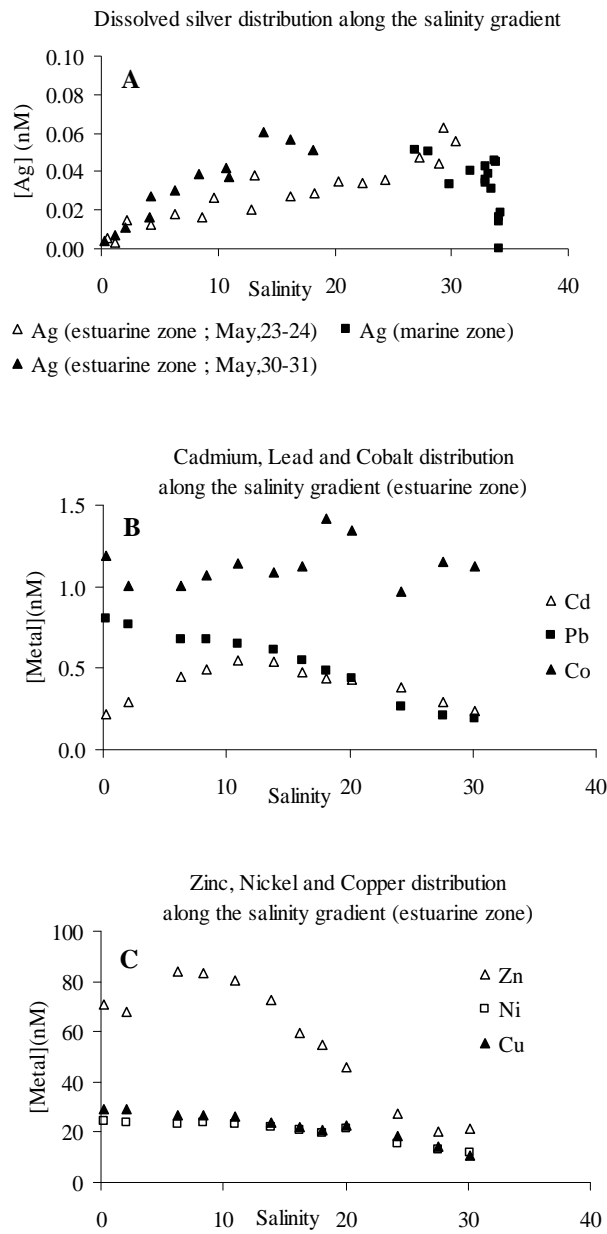


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